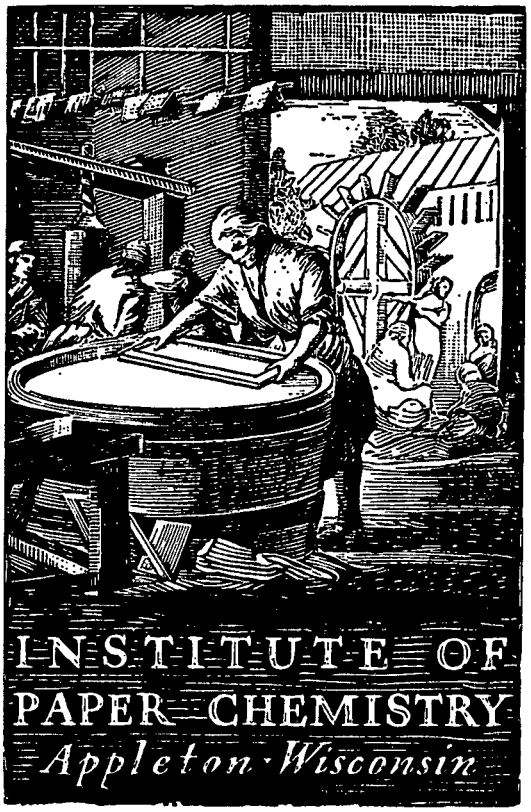

INCREMENTAL CAPACITY IN RECOVERY BOILERS
BLACK LIQUOR BOILING POINT RISE STUDY
Project 3473-4

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

November 24, 1982

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The boiling point rise (BPR) of black liquor implies performance characteristics in evaporation equipment. It may also imply liquor properties. The variation of BPR as solids are increased or as liquor chemistry is altered is the subject of this work.

High solids evaporator design will benefit from the first part. Design and evaluation of liquor pretreatment systems, especially high-intensity liquor oxidation, will benefit from the second part. Oxidative pretreatment is a process designed to yield incremental recovery boiler capacity. Evaluation of this process is covered under a separate report to be issued shortly.

An experimentally based estimate of black liquor (unoxidized) BPR between 40 and 95% solids content shows a continual increase of BPR with solids, the estimated BPR value for 85% solids content liquor being 30°C. The BPR estimate is based on data developed in this project plus other published sources. At the present time the accuracy of the estimate is unknown.

The developed BPR relationship with solids content implies a lower vapor pressure, a higher heat of vaporization, and a negative heat of dilution for black liquor when compared with water.

A literature review revealed that there were no proven published techniques for BPR measurements of highly viscous liquids. One source (10) reported a successful pilot process for achieving dried solids by dispersing black liquor in hot oil.

The oil dispersion concept was developed into an atmospheric pressure-based BPR measurement technique and evaluated in the present study. The required equipment was readily available. However, extensive procedure development and data analysis were required. Two techniques, one for the oil dispersion method and one for an oil-free system, were developed. Unoxidized black liquor was used for this development. One black liquor with three oils (decane, dodecane, and hexadecane) has been studied to date. Both oxidized and unoxidized conditions were studied.

The resultant oil dispersion technique, when coupled with developed oil-free techniques, yields experimental methods for estimating BPR values. These methods, however, are not sufficiently accurate for exacting thermodynamic characterization of black liquor. General trends for these properties are presented.

Imposition of oil into black liquor water vapor systems consistently results in liquid-phase superheat. This superheat imparts significant errors to BPR measurements. Methods were developed that minimized superheat. These appeared to work effectively for liquors above 75% solids content. Below this value inherent superheat differences increased as solids content decreased. Data used for the best-fit BPR estimate below 75% solids content were from oil-free liquor systems.

The upper solids content limit for the experimental technique developed in this work is between 85 and 90%. Within this range the solids settled out of the oil phase as a massive viscous sludge, shearing the agitator safety pin. Data above 85% came from two other sources (10,13), both using pressures above one atmosphere.

BPR estimates for general use can be obtained from the best-fit BPR vs. solids content relationship presented in this report. BPR estimates for a specific unoxidized liquor can be determined via one of the two techniques developed in this

work. Below 65% solids content, oil-free system data are collected. Between 75 and 85% data with the oil dispersion technique is recommended. Between 65 and 75% and above 85% interpolation/extrapolation is necessary. BPR estimates for oxidized liquor can be obtained below 50% solids content in oil-free systems. Between 50 and 63% solids content the oil dispersion technique is recommended. Neither method was successful above 63% solids on oxidized liquor. No further technique development on the oil dispersion method is planned.

Development of an oil-free technique for vapor pressure measurement, implying BPR, is needed. Criteria for the improved technique plus one specific concept are presented. The objective of the new technique would be to develop data, of sufficient accuracy, such that thermodynamic property characterization of black liquor is possible. In addition to more accurate BPR and vapor pressure estimates, heats of vaporization, heats of dilution, phase transitions, and bonding strengths could also be obtained.

INTRODUCTION

Intensive black liquor oxidation is presently under evaluation as a means for achieving additional throughput in a recovery boiler. Liquor oxidation could potentially affect processes before the recovery boiler, i.e., multiple-effect evaporators and concentrators. If liquor oxidation occurs before or between these processes, rheological and thermodynamic properties would be altered. It is well recognized that black liquor oxidation will increase liquor viscosity and, hence, reduce heat transfer rates. There is no reported information on the vapor pressure of oxidized black liquors.

Black liquor vapor pressure is a significant parameter in evaporator and concentrator operation since it determines pressure-temperature (P-T) relationships. The effect of depressed liquor vapor pressure, relative to water, is more commonly expressed as boiling point rise (BPR). The BPR is defined as the difference between the boiling temperature of black liquor and that of pure water at the same pressure (normally 1 atm.).

There is some reason to believe that liquor oxidation may yield lower BPR values. Should this be the case, oxidized liquors will have a larger net thermal driving force than unoxidized liquors. The higher delta T will allow either greater capacity in existing units or require less heat transfer area in new units, all else being equal. If higher BPR values are measured for oxidized liquor, more fundamental chemistry studies would be suggested.

In addition to the direct value of BPR measurements, there are other uses of black liquor vapor pressure data.

1. As black liquor is concentrated, the solubility limit of some of the inorganic constituents is exceeded. Since insoluble material contributes negligibly to vapor pressure behavior, vapor pressure data might serve to identify the onset of precipitation and possibly the degree of supersaturation.

2. Vapor pressure measurements can provide information on the physical-chemical nature of black liquor. This includes heat of vaporization, heat of dilution, and phase transitions.

3. Dried solids vapor pressure measurements would indicate water bonding and hygroscopic characteristics. These data may also be important for interpreting bonding between liquor solids and oxygen when compared with unoxidized liquors. Desirable conditions for dry solids storage would be another result.

There are numerous problems in measuring the vapor pressure of black liquor. Many are viscosity related. The high viscosity of concentrated black liquor leads to poor flow characteristics and inhibited convective transfer operations. Pronounced gradients of temperature and concentration can exist in the liquor. Vaporization rates are generally low. Boiling action does not necessarily eliminate inhomogeneities. In principle, vapor pressure is a thermodynamic property of the black liquor and is determined by establishing an equilibrium between a uniform liquid phase and a uniform vapor phase. Factors leading to nonequilibrium include temperature and concentration gradients resulting from hindered flow, liquor superheat due to suppressed nucleate boiling, and delayed inorganic crystallization. Other problems include difficulty in making accurate measurements of solids contents of the liquor and interference by noncondensable gases (such as air trapped or dissolved in the liquor).

This report presents a literature summary of data and techniques for BPR/ vapor pressure measurements on black liquor and related applications. It further reports on experimental evaluation of one BPR technique that appears applicable to highly viscous black liquors.

BACKGROUND

AVAILABLE TECHNIQUES

Several methods have been developed for measuring vapor pressure of liquids; they are potentially applicable to black liquor. The simplest is a direct measurement of the liquor boiling point. By coupling the boiling vessel to a barastat, a complete P-T relationship can be determined. This method (at atmospheric pressure) is commonly used for measuring BPR of low solids black liquor. Frederick (1) used this technique to measure BPR value on liquor up to 65% solids content. Kobe (2) used this technique plus a bulb condenser and a sealed system to give data under subatmospheric conditions. The highest solids content in Kobe's work was 63%.

The basic problem with this technique for any solution is to eliminate the liquid-phase superheat. Accurate work requires special apparatus. These provide for liquid-vapor equilibrium at the liquid-phase temperature sensor. Typically a Cottrell pump for liquid recirculation is employed. Such apparatus are successful on low-viscosity one- or two-component miscible systems (3,4,5). Highly viscous black liquors lead to pronounced superheat levels in the liquid phase. Cottrell pumps are inoperable under these conditions. It is doubtful if normal ebulliometric apparatus would be successful on any black liquors beyond 65-70% solids content.

Ziegler (6), who faced similar viscosity problems with sugar solutions, proposed an alternate to direct liquid-phase measurements. His approach was to measure the vapor temperature immediately above the boiling liquid. The evolved vapors should have a temperature representing the average liquid-phase temperature. The fragile vapor could, however, be superheated or quickly cooled. This approach is not the answer to analytical BPR measurements.

Sotobayashi (7) developed a rotating twin-ebulliometer that eliminates the need to pump the liquid phase. This apparatus was found useful for BPR measurements of polystyrene dissolved in benzene where foaming had previously been a problem. His technique may have application to weak black liquors which readily foam. Its performance with highly viscous liquors is doubtful unless a thin liquid-phase film can rapidly equilibrate with the vapor.

Kobayashi (8) developed a high-temperature vapor pressure measurement technique which included pumping evolved vapors back into the equilibration chamber. Although he studied only relatively low-viscosity organic compounds, some variation of this technique may provide the most accurate data. Special apparatus and procedure development would be required for application to highly viscous black liquors. An interesting aside is that he claims potential noncondensables and dissolved gases were removed by repetitive freezing and thawing prior to experimentation.

Funk (9) measured vapor pressure under static conditions by placing a vessel containing liquor and a connecting pressure sensor in a constant temperature environment. A mercury manometer sensed pressure and an air hot box maintained temperature. Funk had great difficulty in obtaining good data because of sealing problems associated with extended times at high temperature. A subsequent error analysis of this approach indicates that to get thermodynamic properties within 10% the pressure measurement needs to be accurate within 1% and the temperature accurate within 0.3°C. The required accuracy and stability in the temperature are beyond the capability of the air hot box used. Direct vapor pressure measurements are very sensitive to error from noncondensable gases, since these will contribute to the total pressure measurement. Although these problems can be minimized by cycling through a number of evacuations and measurements, the persistence with which air can

be held in black liquor and the possible release of other volatiles leave noncondensables as a serious potential problem for any direct P-T measurement technique.

One pilot process technique that has been successfully used to concentrate black liquor all the way to dryness is dispersion in an immiscible liquid (oil) (10). A similar approach can be used for vapor pressure measurements. The measurement is obtained by placing a refluxing condenser above a pot containing boiling black liquor and oil. The system operates at atmospheric pressure. One temperature sensor measures the boiling temperature in the pot, and another measures the temperature of the refluxing condensate which is equilibrated with the rising vapor. This method is potentially operable up to dry solids and is insensitive to the presence of noncondensable gases.

One inherent problem with the oil dispersion technique is enhanced liquid-phase superheat. Swietoslawski (3) points out that boiling point measurements with two immiscible liquids are subject to even greater superheat errors than miscible systems. Separation and reequilibration of the two phases is essential to remove the inherent superheat from the more volatile component. Special apparatus are required for this purpose (3). Separation of the two phases would not be practical in a liquor-oil system since viscosity problems would resurface. The requirement of this technique, then, is to find an oil which provides the needed fluidity while minimizing liquid-phase superheat.

Isopiestic methods are another approach. If vessels containing two different solutions are placed side by side in a closed space, vapor will distill from the higher vapor pressure solution to the lower one. At equilibrium, the vapor pressures of each will be equal. If the vapor pressure of one solution is known as a function of concentration and temperature, the other is then determined. This

approach is insensitive to the presence of noncondensable gases (although they may increase equilibration time) and total pressure. It requires only a known standard solution and measurement of the equilibration temperature and concentrations. This approach has the potential for giving very accurate data. However, equilibration periods may exceed 24 hours. The extended times could alter the liquor crystalline characteristics. Special apparatus and extended procedure development are necessary.

Published Data

Black liquor BPR data from six different sources are given in Fig. 1. Since different liquors were used in these studies, only general comparisons can be made. TAPPI Monograph 32 is a widely used source of BPR data, especially for lower solids liquor. This curve was developed by Han (11) and is based heavily on neutral sulfite liquors. Han found close agreement with three kraft black liquor (western hemlock) points measured by Kobe (2). This led Han to suggest that the entire curve is applicable to kraft liquors. Recently Frederick (1) published BPR data at solids contents up to 65%. Arhippainen (12) reported BPR data for Finnish pine kraft black liquor. Although the experimental approach was not described, it was probably similar to that of Frederick.

A BPR value of 80% solids black liquor is implied within the process specifications for a high-solids thin-film evaporator described by Andrews (13). This is a best-fit value from data generated in various bench and small pilot scale apparatus. Subsequently, an additional point at 88% solids was obtained from the same source.

Clay (10) reported BPR values for black liquors exceeding 95% solids content. The oil dispersion technique, discussed earlier, was used.

Funk (9) measured the vapor pressure of black liquor directly at various solids levels and calculated BPR values from the vapor pressure vs. temperature

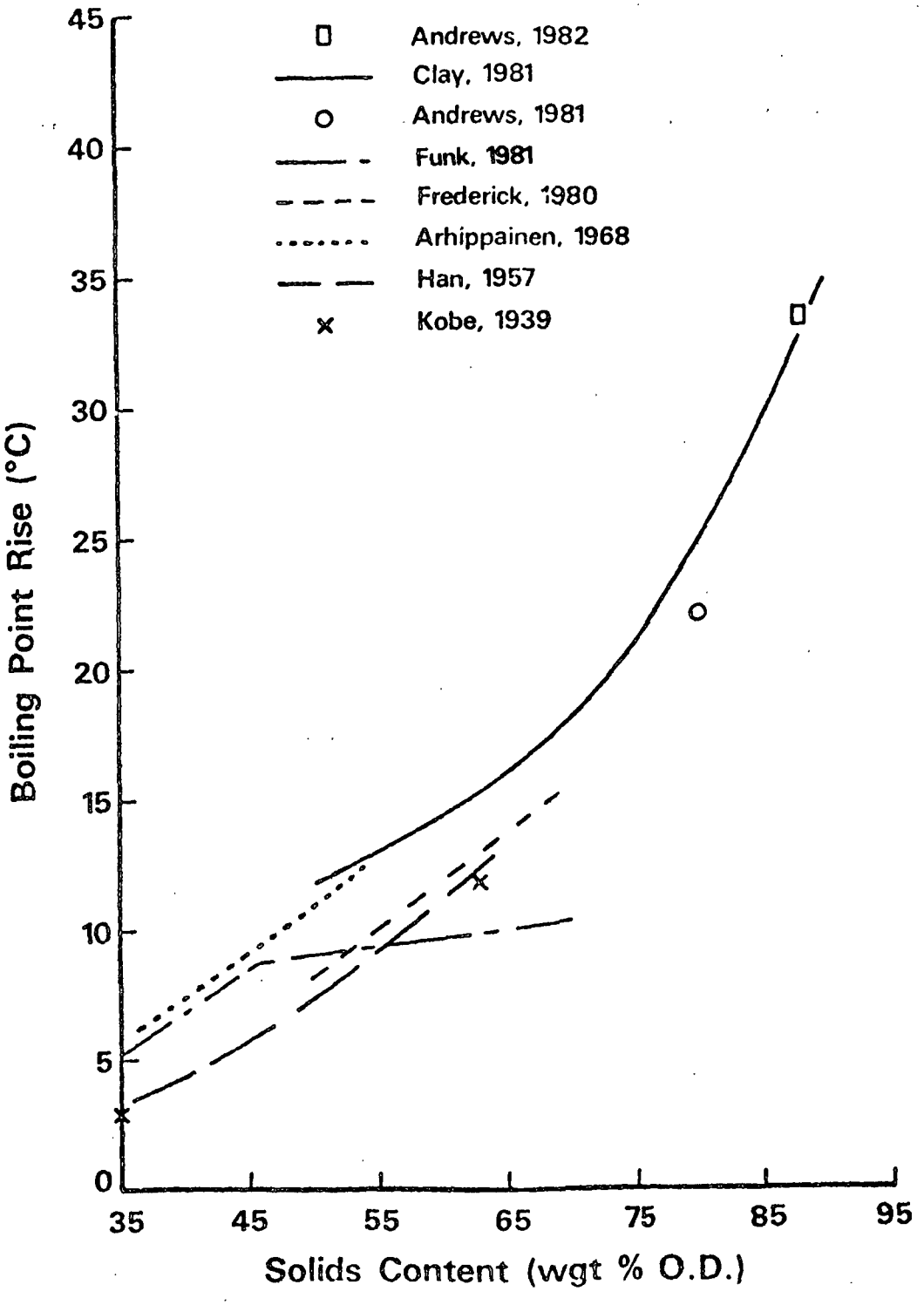


Figure 1. Kraft liquor boiling point rise data from published data.

curves. Long times (more than 24 hours) were needed to reach static equilibrium. These data deviate considerably from the general trends exhibited by all of the other data, possibly because the long times involved allowed inorganic precipitation to proceed to completion. However, there are serious questions concerning the validity of these data because of leakage problems and complications from noncondensable gases.

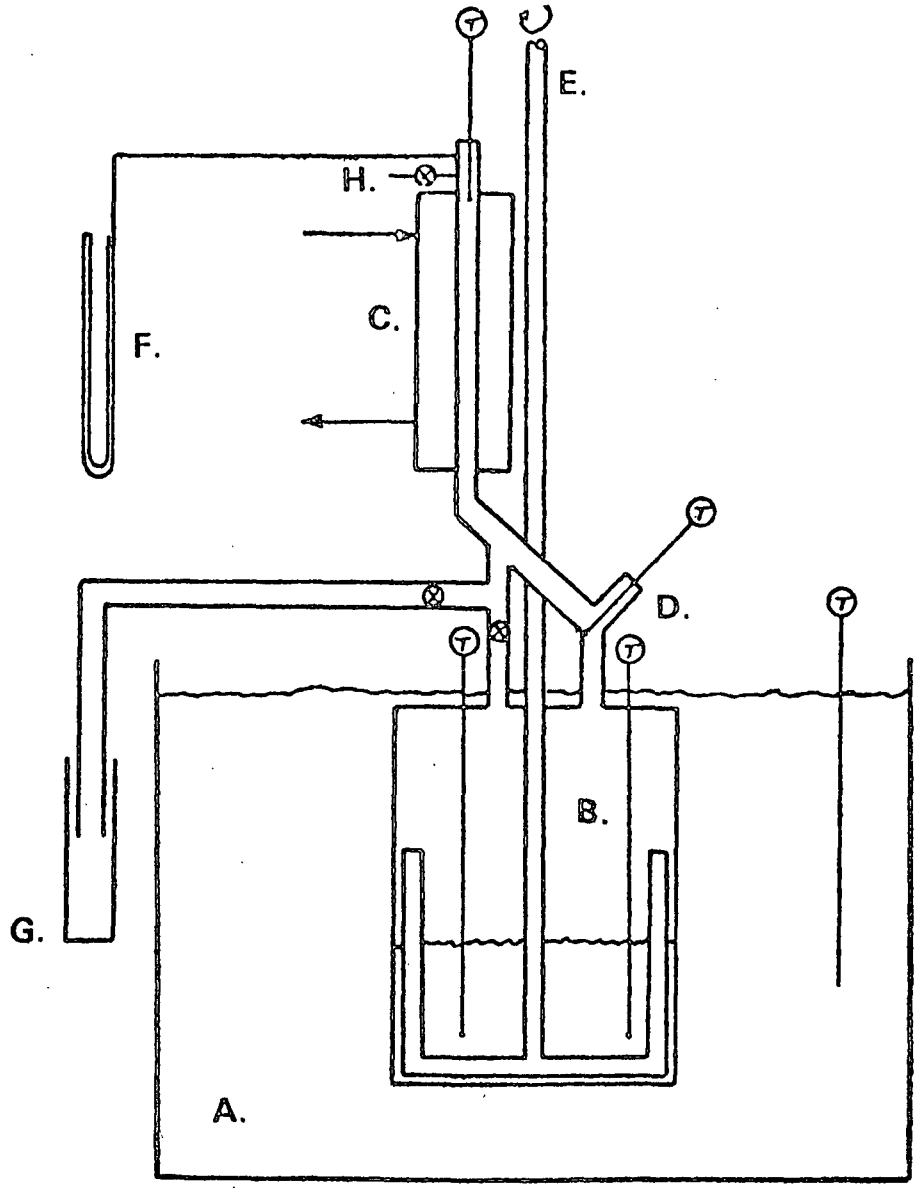
With this exception, all data in Fig. 1 show a continually accelerating increase in BPR as solids increase. There is good agreement between the data of Clay and those of Andrews at solids contents above 70%. Extrapolation of Frederick's and Kobe's data would also seem to be consistent with these trends. Clay's data appear high at solids contents below about 65%. The significance of this will be discussed later.

EXPERIMENTAL

APPROACH

The BPR measurement technique chosen for evaluation was oil dispersion similar to that implied by Clay (10). It is the only reported technique for highly viscous systems and required minimal equipment development. Extensive procedure development, however, was required. The partial pressure of water vapor in the system can be altered by selecting oils of differing volatility. When the water partial pressure is changed in this manner, all runs can be made at a convenient constant pressure. Atmospheric pressure was chosen to minimize problems associated with leaks and noncondensable gases.

The experimental apparatus is shown in Fig. 2. The vessel has a volume of 3.7 liters. The agitator speed was on the order of 100 rpm. The entire vessel was submerged in a temperature-controlled oil bath. Two type-J thermocouples were immersed in the liquid phase just above the agitator. The condensing temperature was measured by a thermocouple positioned in an uninsulated glass Y section immediately above the oil level in the bath. The thermocouples were connected to a digital readout sensitive to 0.06°C (0.1°F). The thermocouples and readout were calibrated against a standard National Bureau of Standards thermometer. The resultant thermocouple calibrations were accurate to within $\pm$ 0.2°C ($\pm$ 0.4°F). The condensate bypass return or removal point was immediately above the Y section. A water-cooled glass condenser, vented to a water manometer open to the atmosphere, was used. During start-up, noncondensables are vented to the atmosphere through a valve located between the condenser and manometer.



A. Temperature controlled oil bath.
B. 3.7 liter vessel.
C. Water cooled condenser.
D. Y ambient cooled condensing section.
E. Agitator.
F. Water manometer.
G. Collection of condensed Condensate.
H. Noncondensable vent.

Figure 2. Boiling point rise experimental apparatus.

The following data were recorded.

1. Two temperatures of the liquid phase in the vessel
2. Condensing temperature in the Y
3. Atmospheric pressure (mercury barometer)
4. System differential pressure (water manometer)
5. Visual observation of condensation
6. Oil bath temperature
7. Condenser top vent temperature

The initial solids in the black liquor were measured by an extended surface oven-drying procedure. Intermediate and final solids were calculated, based on the total liquor charged and the amount of condensate removed.

PROCEDURE

The vessel was typically charged with 400 g of black liquor and 750 g of oil. It was then immersed in the heated bath. The bath temperature was increased until vigorous boiling occurred in the system. The vent valve was open to purge noncondensables until condensing was observed in the glass Y. After condensing had extended into the condenser, the bath temperature was slowly reduced. Data were taken periodically during this cooling step. As the system cooled, the saturated vapor temperature was reached in the Y. This temperature was generally more stable and lasted for a longer time than temperatures under superheat or subcooled conditions. Typically this was when condensation was absent in the condenser but present in the Y.

Liquid-phase cooling is essential to minimize superheat. As the system cooled, the vapor temperature dropped suddenly, signaling loss of condensate in the Y. This was always checked visually. The liquid-phase temperature would then

very slowly decrease. The liquid-phase temperature, at the time of no visually observed condensate in the Y section, was taken as the boiling temperature for BPR calculations.

Higher solids were produced by increasing the bath temperature and withdrawing condensate after condensing had begun and the system had a positive pressure. A measured amount of condensate was withdrawn. Any oil which vaporized and condensed was returned to the vessel. The system was sealed through the water manometer. The cooling cycle was initiated to obtain the desired dynamic equilibrium temperature measurements. Successively higher solids contents were obtained by repeating this sequence.

MATERIALS

Three straight chain hydrocarbon oils with known vapor pressure characteristics were selected. These were:

Hexadecane	$C_{16}H_{34}$
Dodecane	$C_{12}H_{26}$
Decane	$C_{10}H_{22}$

(Reagent grade. Obtained from Aldrich Chemical Co.)

Table I presents their temperature-pressure characteristics. The assumption that these oils are immiscible with black liquor was confirmed by experimental observations.

Black liquor was obtained from Thilmany Pulp & Paper Company at a solids content of 42.8%. Data on liquor analysis are listed in Table II.

TABLE I

TEMPERATURE - PRESSURE RELATIONSHIPS FOR EXPERIMENTAL OILS AND WATER

	Temperatures, °C[a]			Constants for Eq. (7)		Range of Data for Correl., °C	Comparison Prediction vs. Actual		
Pressure, mm Hg	20	200	760	C_1	C_2		P_A	P_P	Δ%
Hexadecane	164.7	231.7	287.5	-8331.68	22.0209	105.3 to 164.7	20.00	19.80	-1.0
Dodecane	104.6	167.2	216.2	-6262.73	19.5504	47.8 to 167.2	20.00	19.40	-3.0
Decane	69.8	128.4	174.1	-5379.69	18.6884	55.7 to 174.1	60.00	59.71	-0.48
Water	--	--	100	-5014.16	20.0709	60 to 120	760.00	756.05	-0.52

[a]Data taken from Ref. (14). More data from same source used for correlation.

TABLE II

BLACK LIQUOR USED IN BPR STUDIES

(Obtained from Thilmany Pulp & Paper Company)

Total	Percent Based on Direct Solids
Na	17.5
K	2.0
Cl	0.3
Active Alkali (as Na_2O)	5.8

Initial system runs were made with distilled water, and aqueous solutions of NaCl and NaOH.

ANALYSIS

Thermodynamic analysis of the oil dispersion technique is as follows. If two volatile immiscible liquids are equilibrated with their vapors, the total system pressure will be the sum of the vapor pressures of the two liquids. In the boiling vessel:

$$P_T = P_{BL}(T_B) + P_O(T_B) \qquad (1)$$

(See Appendix A for nomenclature definition)

In the refluxing condenser:

$$P_T = P_W(T_C) + P_O(T_C) \qquad (2)$$

Solving (1) and (2) for the black liquor vapor pressure:

$$P_{BL}(T_B) = P_W(T_C) + P_O(T_C) - P_O(T_B) \qquad (3)$$

For relatively low volatile oils the difference in oil vapor pressure between the two temperature conditions, i.e., the last two terms in Eq. (3), is small compared with the vapor pressure of water. Under these conditions:

$$P_{BL}(T_B) \cong P_W(T_C) \tag{4}$$

This approximation becomes even more exact when low volatile oils are used with high BPR systems, e.g., high solids, such that large differences in T_B and T_C occur. Direct temperature measurements then should closely approximate the BPR.

$$\text{with:} \quad P_{BL}(T_B) \cong P_W(T_C) \cong P_T \tag{5}$$

$$\text{then:} \quad BPR \cong T_B - T_C \tag{6}$$

When oils with significant vapor pressures are used, Eq. (3) must be solved directly to give black liquor vapor pressure. The first term, $P_W(T_C)$, is readily obtained from the steam tables. The last terms, $P_O(T_C)$ and $P_O(T_B)$, can also easily be determined if pure component oils with known P-T characteristics are used. The experimental measurements required are T_C and T_B.

Pressure-temperature relationships for the oils, water, and various aqueous solutions of NaCl and NaOH were developed using the form

$$\ln P = C_1 \frac{1}{T} + C_2 \tag{7}$$

(Constants are given in Table I)

In a similar manner, when significantly volatile oils are used, the simple relationship of Eq. (6) does not correctly predict the black liquor BPR. BPR measurements are normally obtained at a constant total pressure of the single vapor

component, e.g., water. The partial pressure of water over a black-liquor oil solution will be different than the partial pressure of water at the point of vapor condensation in spite of the fact that the total pressure is the same at both points.

BPR values should be calculated from liquid and vapor temperatures at the same equilibrium partial pressure of water. That is,

$$BPR(P_{BL}) = T_B(P_{BL}) - T_C^*(P_W) \tag{8}$$

where: $P_W = P_{BL}$

T_C^* = Steam table saturation temperature at pressure P_W

If Eq. (6) is used instead of Eq. (8), especially on significantly volatile oils, predicted BPR values will be too low.

The heats of vaporization and dilution can be obtained from an analysis similar to that shown by Funk (9). The summary equations are:

$$\Delta H_{v,BL} = -R \cdot \frac{d\ (\ln P)}{d\ (1/T)} \tag{9}$$

$$\Delta H_D = \Delta H_{v,W} - \Delta H_{v,BL} - \Delta Cp \cdot BPR \tag{10}$$

Extreme accuracy is required in T and P measurements when Eq. (9) is used. This was mentioned earlier in a discussion of Funk's (9) data. Mosselman (15) has recently developed an exact integral solution to the Clapeyron equation, Eq. (9). He claims this solution is 1-2 orders of magnitude less sensitive to P-T data deviations than the differential form. This may be an approach to pursue with future work.

RESULTS

STANDARD SOLUTION RUNS

Initial tests were run with distilled water and standard solutions of NaOH and NaCl. A check on the accuracy of the results was complicated by a divergence in published data (16,17). Dewey (18) presents a regression equation for the BPR of NaOH based on reference (16) data. He apparently thought these data were more exact. The published data plus data from this work are displayed in Fig. 3. Table III presents the experimental BPR values plus the implied vapor pressure for the various solutions.

Test results for NaCl solutions are presented in Fig. 4 and Table III. The solubility limit for NaCl is approximately 28.5% by weight at 100°C (14). Note the expected flattening of the curve beyond this point in Fig. 4. It is encouraging to note this behavior in the presence of oil.

For both NaOH and NaCl the measured values were above those of the published data. In the oil-free NaOH system the deviations increased with solids content. The NaCl oil-free system showed closer agreement with the published data. In both systems addition of oil increased the observed BPR. Table IV summarized these deviations. Reasons for deviations in oil-free systems from the published data are unclear. The relatively constant deviation of +0.8°C when oil is added is due to liquid-phase superheat. This has been mentioned earlier and will be discussed later in the context of all results.

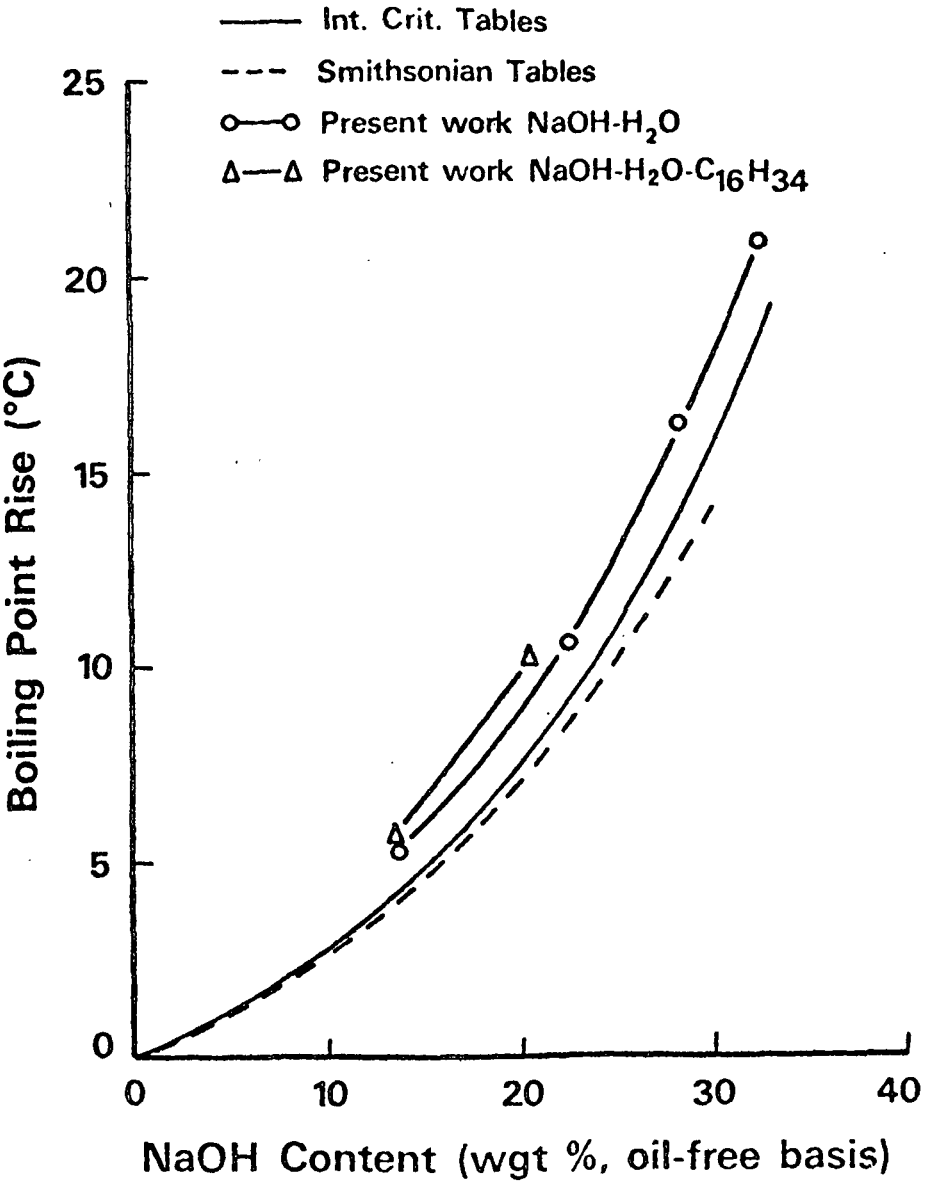


Figure 3. Sodium hydroxide boiling point rise data.

TABLE III

BOILING POINT RISE DATA AND VAPOR PRESSURE
OF STANDARD SOLUTION RUNS

Run No.	System	Solids, wt.%	T_B, °C	BPR,[a] °C	$\hat{P}_{SOLN}(T_B)$,[b] mm Hg
1	H_2O-NaOH	13.7	104.7	5.3	740.4
		22.5	109.9	10.6	740.4
		28.3	115.7	16.2	740.4
		32.7	121.3	21.9	740.4
2	H_2O-NaOH	13.7	105.1	5.7	739.3
	$-C_{16}H_{34}$	20.5	109.6	10.2	739.0
4	H_2O-NaCl	17.4	104.7	5.7	730.9
	$-C_{12}H_{26}$	19.6	105.2	6.1	730.5
		22.4	106.1	7.1	729.7
		27.5	108.2	9.3	727.7
7	H_2O-NaCl	16.7	103.4	4.6	725.9
	$-C_{12}H_{26}$	22.5	105.6	6.8	724.1
		27.6	107.8	9.1	722.0
13	H_2O-NaCl	17.5	104.3	5.3	729.6
	$-C_{12}H_{26}$	20.0	105.1	6.1	729.0
		23.0	106.4	7.5	727.8
		27.5	108.4	9.6	725.9
		30.3	108.7	9.8	725.7
		35.3	108.4	9.6	725.9
		40.3	108.4	9.6	725.9

[a]Calculated via Eq. (8).
[b]Calculated via Eq. (3).

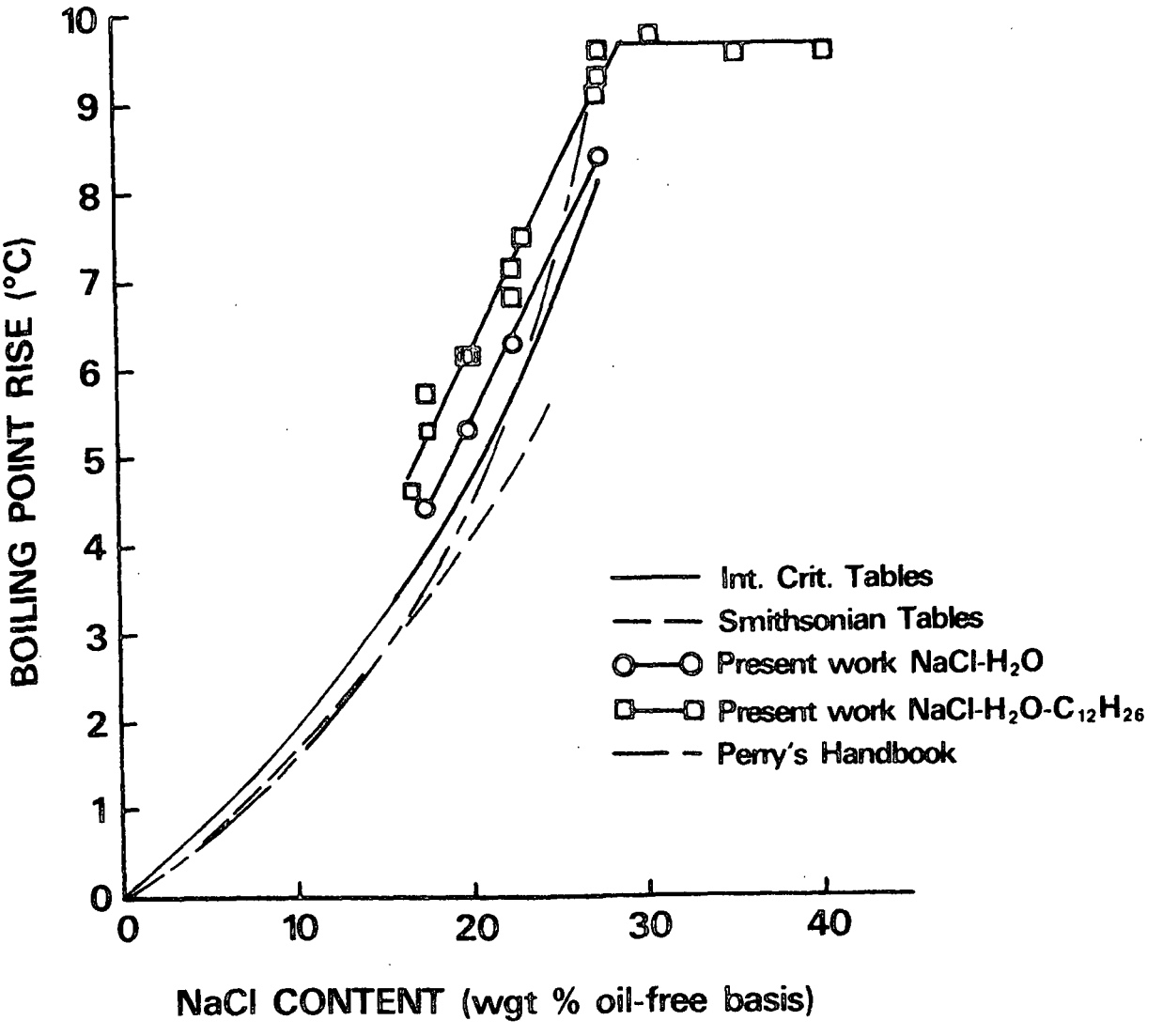


Figure 4. Sodium chloride boiling point rise data.

TABLE IV

DEVIATIONS OF MEASURED STANDARD SOLUTION
BPR VALUES FROM REFERENCE (16) DATA

System	Solids, %	BPR_m-BPR (18), °C	ΔBPR Due to Oil, °C
H_2O-NaOH	15	+1.2	--
	20	+1.4	--
	30	+2.0	--
H_2O-NaOH-$C_{16}H_{34}$	15	+2.0	+0.8
	20	+2.3	+0.9
H_2O-NaCl	17.5	+0.5	--
	22.0	+0.8	--
	27.5	+0.3	--
H_2O-NaCL $C_{12}H_{26}$	17.5	+1.3	+0.8
	22.0	+1.6	+0.8
	27.5	+1.1	+0.8

Black Liquor Runs

Measured values of BPR for the black liquor are shown in Fig. 5. Table V lists the BPR values and implied liquor vapor pressures. Two points listed in Table V were not used. These will be discussed later. With this exception, these data agree in magnitude and shape with the published data of Fig. 1 at the higher solids contents. In particular, the data of Andrews (13), Clay (10), and the present work all show the accelerated BPR rise with increasing solids content. Extrapolation of Frederick's (1) and Kobe's (12) data would also suggest the same trend. This is in marked contrast to the results of Funk (9) where flattening of the BPR curve occurred above 50% solids content. BPR curve flattening could be explained if crystallization, analogous to NaCl in Fig. 4, occurred. In dynamic liquor systems this apparently does not occur.

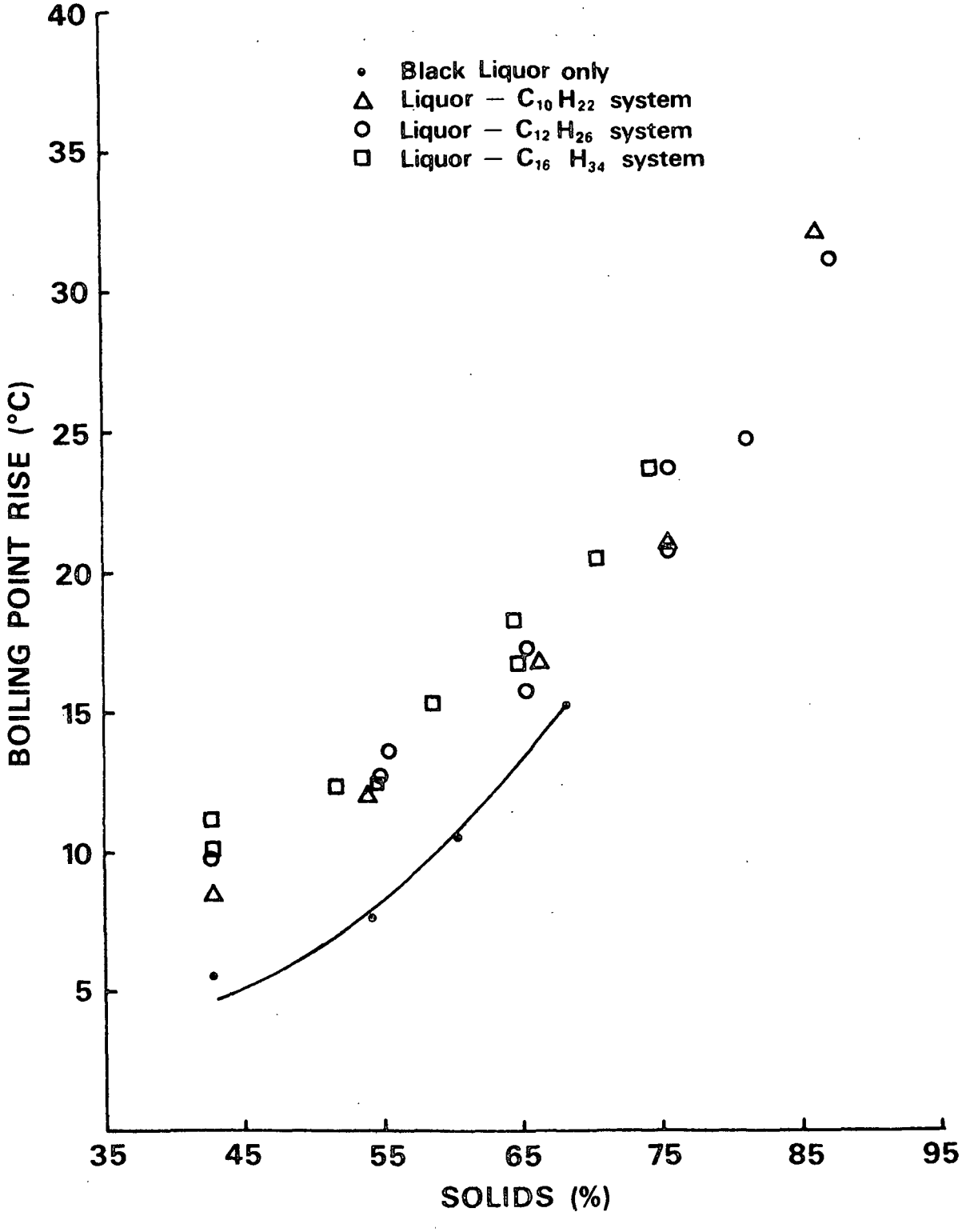


Figure 5. Black liquor boiling point rise data from this work.

TABLE V

BOILING POINT RISE DATA AND VAPOR PRESSURE OF BLACK LIQUOR

Run No.	System	Solids, wt. %	T_B, °C	BPR,[a] °C	$P_{BL}(T_B)$,[b] mm Hg[b]	
5	Liquor-$C_{12}H_{26}$	42.8	108.3	9.8	717.0	
		54.8	111.1	12.7	714.1	
		65.3	114.0	15.7	710.8	
		75.7[c]	118.7	20.7	704.5	
		81.4[c]	122.6	24.7	700.2	
		87.4[c]	128.6	31.2	689.1	
6	Liquor-$C_{10}H_{22}$	42.8	105.2	8.4	674.0	
		54.0	107.8	12.0	648.7	
		66.2	111.8	16.7	633.4	
		75.5[c]	115.5	21.0	617.7	
		86.1[c]	124.4	32.0	571.7	
8	Liquor-$C_{12}H_{26}$	42.8	108.7	10.0	719.8	
		55.4	112.1	13.6	716.2	
		65.4	115.6	17.2	711.9	
		75.9[c]	121.7	23.7	703.2	
		85.0	136.4	39.7	672.5	(data point not used)
9	Liquor	42.8	105.0	5.5	742.5	
		49.7	107.1	7.6	742.5	
		60.5	110.9	11.2	746.5	
		68.2	114.7	15.1	746.5	
11	Liquor-$C_{16}H_{34}$	42.8	109.7	10.0	746.4	
		51.8	112.0	12.3	746.2	
		58.5	114.8	15.2	747.5	
		64.5	117.8	18.2	747.2	
		70.4	120.0	20.3	746.9	
12	Liquor-$C_{16}H_{34}$	43.0	110.7	11.1	743.4	
		54.8	112.0	12.4	743.3	
		64.9	116.2	16.7	742.9	
		74.5	122.9	23.6	737.7	
		80.7	134.1	34.8	735.6	(data point not used)

[a]Calculated via Eq. (8).
[b]Calculated via Eq. (3).
[c]Data used for Fig. 6.

At lower solids content, less than 75%, the present data with oil are significantly higher than in the oil-free liquor systems. This is a trend analogous to the oil-liquor system data of Clay (10). Neither oil-liquor system's data extrapolate to zero BPR at infinite dilution. Both NaOH and NaCl in oil systems, Fig. 3 and 4, have a reasonable extrapolation to zero. A separate test was run to check the influence of the oil to solids ratio on measured BPR. The data are presented in Table VI and Fig. 6. The trend displayed in Fig. 6 clearly shows that BPR values at lower solids content increase as the oil to solids ratio increases. The implication is that liquor-oil systems should not be used for measuring BPR in liquors of medium solids content. This will be discussed further in the next section.

BPR measurements made on partially oxidized Thilmany black liquor are presented in Table VI and Fig. 7. The degree of oxidation was between 7.0 and 7.5% of the total oxygen demand. The comparison with unoxidized liquor in Fig. 7 shows significantly higher BPR values for oxidized liquor at the same solids content. The trend of higher BPR values in a liquor-oil system than in an oil-free system, is again observed at the lower solids. The upper point in the oil-free system (connected to the others by a dashed line) is questionable. Significant moisture gradients may have been present since system fluidity was dramatically reduced. This is discussed in more detail in the Observations Section. The best measure of BPR for oxidized liquor is the oil-free data below 50% and the liquor-oil system data above 50%.

OBSERVATIONS

The most pronounced characteristic of oil-aqueous systems is the tendency to sustain substantial superheat. Swietoslawski's (3) comments were indeed correct.

TABLE VI

BOILING POINT RISE DATA AND VAPOR PRESSURE OF BLACK LIQUOR

Run No.	System	Solids, wt. %	T_B, °C	BPR,[a] °C	P_{BL} (T_B),[b] mm Hg	
15		(43.1	105.2	5.7	743.0	liquor only)
	Liquor-	43.1	106.6	7.1	742.9	
	$C_{16}H_{34}$	45.5	107.8	8.3	743.1	
	(O/S = 1.3)	50.6	109.0	9.5	743.0	
		55.7	111.2	11.7	743.0	
		65.4	114.9	15.4	742.7	
16	Liquor	43.1	107.4	7.7	749.5	
	(oxidized)	50.0	112.0	12.3	749.5	
		54.8	120.8	21.1	749.5	
17	Liquor	42.8	111.1	11.4	746.8	
	(oxidized)	50.0	111.4	11.7	746.8	
	- $C_{16}H_{34}$	55.1	115.6	15.9	746.4	
		59.9	120.0	20.4	745.9	
		62.2	125.1	25.5	745.2	

[a]Calculated via Eq. (8).
[b]Calculated via Eq. (3).

Two levels of superheat were observed. The initial level is the temperature difference between a vigorously boiling oil-liquor system and the same system at dynamic quiescent boiling described in the Procedure Section. It was possible to obtain up to 13°C of this observed superheat in certain oil-liquor systems. High superheats such as this occurred at high solids. This initial superheat, however, could be easily removed from experimental data via the developed methods.

The second level of superheat appears inherent to oil-liquor systems. It represents the temperature difference between an oil-free system and an oil system with the same liquor. Unlike the first level, this could not be removed via the experimental methods developed to date. This is the type observed earlier with NaCl

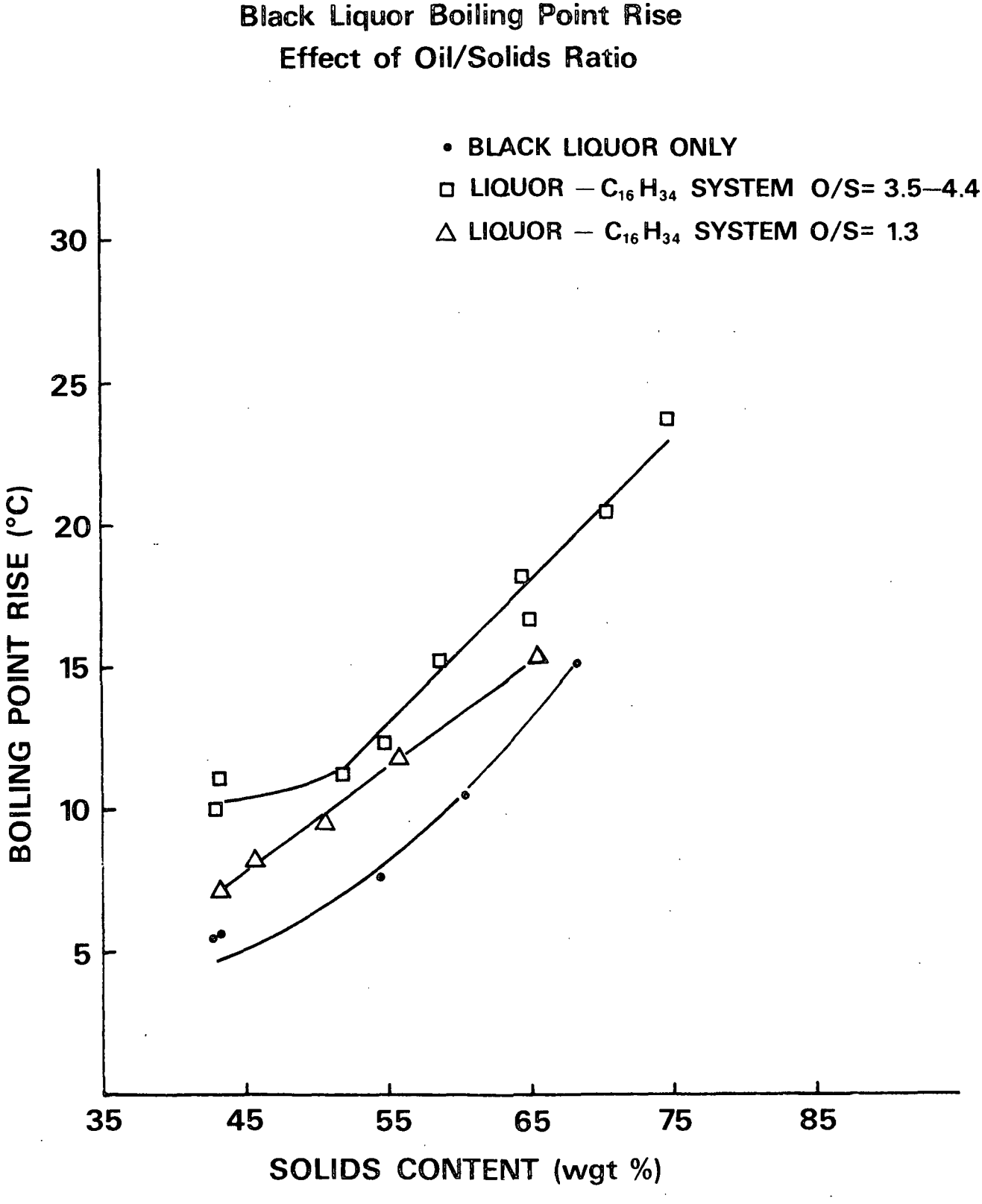


Figure 6. Effect of the oil to solids ratio (O/S) on BPR measurement.

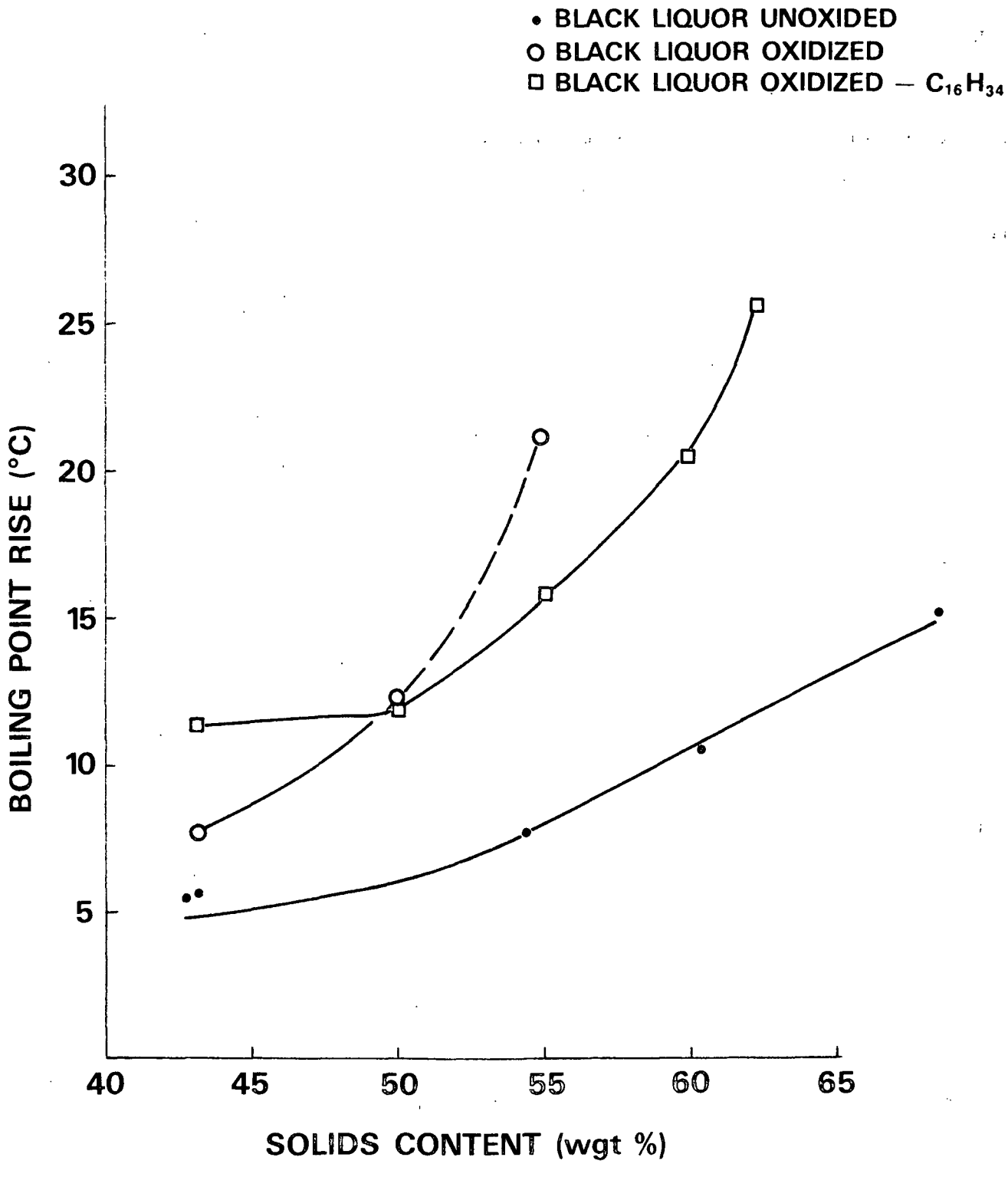


Figure 7. Comparison of BPR measurements between oxidized and unoxidized liquor.

and NaOH systems. The level for black liquor can be observed via Fig. 5. Oil-free BPR values are typically 5°C below oil dispersion data at 45% solids content. At 65% solids content the difference has decreased to 2-3°C. Extrapolation of the oil-free curve suggests minimal problems from superheat above 75%. There were, however, some repeatability problems at higher solids contents. These will be discussed later.

The larger difference at lower solids may be related to the dispersion characteristics of liquor in oil. The lower solids content implies liquor that is less viscous and hence easier to disperse. The resultant droplets would be small. Enhanced surface tension forces may inhibit normal P-T characteristics. Reid (19) reports that bubble nucleation rates decay exponentially with increasing liquid surface tension raised to the third power. Reduced nucleation rates encourage superheat.

As the solids increase, so does the viscosity. When particles impact each other at the higher viscosity, they may agglomerate and not dissipate as before. The larger particles are not subject to the surface tension forces of smaller particles and, hence, may more closely approximate true P-T behavior. The higher the solids, the better the estimate. Surface tension also increases with solids content but apparently not as fast as viscosity-related particle growth.

Experimental methods tested to eliminate this inherent superheat included changes in agitation speed and liquid level. Neither had any pronounced effect. Both measurements of liquid-phase temperature were consistently in agreement.

The majority of runs were with oil/liquor solids weight ratios of 3.3 to 4.4. Two runs were conducted at a ratio of 1.3. Both consistently showed lower BPR

values than runs with a higher ratio. The data presented earlier in Table VI and Fig. 6 are from the second of these two runs. These data support the above discussed hypothesis. In short, liquor dispersed in oil (high O/S) will have an inherently higher degree of liquid superheat than oil dispersed in liquor (low O/S).

Boiling only water in the system showed a superheat level of 0.1-0.2°C above equilibrium. The equilibrium temperature was within 0.1°C of that predicted from the correlation in Table I at the given atmospheric pressure. When dodecane was added to the water, a liquid superheat of 0.5°C was maintained at equilibrium.

With NaOH and NaCl oil systems the superheat difference between vigorous boiling and equilibrium was 0.5°C. Boiling liquor alone at 68% solids content showed a superheat of 1°C when cooled to equilibrium. Cooling from the vigorous boiling condition to quiescent dynamic equilibrium, as outlined in the Procedure Section above, is essential for all systems in this work. Alternate methods for removing superheat from the liquid-phase temperature measurement have been discussed earlier.

The temperature recorded in the Y section varied considerably, corresponding to contact with superheated vapor, saturated condensing vapors, subcooled condensate, and hot condensable gases. With vigorous boiling, superheated vapors were present. Mild boiling gave saturated condensed vapor. Low or no boiling resulted in the latter two conditions. The immiscibility of the water and oil was clearly seen in the condensate for all runs, more so with the volatile solvents.

Black liquor solids contents greater than 90% were not obtained in this work. Between 85 and 90% solids the liquor settled to the bottom in a mass. The liquor then became viscous enough to shear the safety key in the agitator drive.

The resulting liquor was a tarlike mass that quickly hardened on cooling and separated from the oil. A modified procedure and agitator design coupled with increased turbulence may allow for measurements at 90% solids or greater.

The oxidized liquor tested had markedly higher viscosities than the unoxidized liquor. The loss of fluidity at 54.8% solids content in Fig. 7 was due to viscosity. The agitator slowed down. Addition of condensate, equivalent to 53.8%, produced acceptable fluidity. With the oxidized liquor-oil system operable conditions were achieved up to 62.2%. Although the test equipment is not set up to measure viscosity, its performance suggests that oxidized liquors at 60-65% solids content have viscosities comparable to unoxidized liquors at 80-85% solids content.

The liquid-phase temperature recorded when the presence of condensate was just lost in the Y was used for determining BPR. Occurring simultaneously with the loss of condensate was an increase in system vacuum and a rapid decay in vapor temperature. Typically the exterior oil bath temperature was within 2°C of the liquid-phase temperature so that heat transfer to and from the vessel should be minimal.

Vapor temperature values most consistent with calculated dew points for the oil-aqueous systems occurred when condensing occurred only in the Y section. When condensation extended into the condenser, superheated vapor gave excessively high temperatures.

The critical conditions for vapor and liquid temperature measurements did not occur at the same time. For this analysis the liquid temperature used for calculating BPR was that measured when condensing was first lost. The vapor temperature used was that calculated from known water and oil vapor P-T relationships,

i.e., Table I. This value was observed experimentally as the system cooled from boiling to equilibrium.

Data Accuracy

The two liquid-phase temperature measurements in the NaCl-oil system, when corrected via NBS calibration, were typically within <0.1°C of each other. For liquor-oil systems they agreed to within <0.2°C.

The vapor-phase temperature via correlations from Table I and Eq. (2) is predictable to within <0.2°C. This is based on the water vapor pressure correlation, since it is the major vapor component. The greatest swing in barometric pressure noted during any one run was 1.3 mm Hg. The corresponding temperature swing was <0.1°C.

The temperature measurement equipment was calibrated as mentioned earlier. Its accuracy was ± 0.2°C.

Measurements were not made to check the oils' P-T characteristics against the published data (14).

It is obvious from the above that the greatest temperature sensing inaccuracies result from the liquid-phase superheat phenomena. Its magnitude has previously been discussed. At lower solids it is fairly reproducible. No one oil produced inherently lower superheat levels. A number of heating/cooling cycles at a given solids content in an oil-liquor system produced the same results. At the higher solids such was not the case. The two data points in Table V that were deleted from analysis are an exception. For some reason excessively high BPR values were generated in these runs.

The initial solids content of the liquor was 42.8 ± 0.1%. The condensate removal measurement accuracy was good to within 1-2 grams. The major limit was the ability to quantitatively separate condensate from the vaporized oil. At the lower solids levels, possible errors could be 0.5% solids units. At the higher solids levels, errors of as much as 3% solids units may be possible. This alone may also explain the apparent low level of repeatability at higher solids content and the two points in error above. The other factor is the highly sensitive couple between BPR and surface tension at the higher solids contents.

Several runs concentrated liquor to high solids, then diluted it back to the initial solids. Repeatability at a given solids content was never extremely poor but, with one exception, was better at solids less than 55%. Several of these so-called hysteresis runs involved shutting down at night and restarting the next day. No problems with this procedure were found.

DISCUSSION

BPR ESTIMATE

Because of inherent superheat problems at lower solids content, data from only the greater than 75% solids content oil-liquor systems should be used. The oil dispersion technique below this solids content for unoxidized black liquor predicts excessive BPR levels.

The best estimate of unoxidized black liquor BPR at high solids is presented in Fig. 8. Six points from this work's oil-dispersion runs, noted in Table V, are combined with this work's liquor run, Andrew's (13) two data points, and the best-fit line from Clay (10) to obtain the estimate.

The best estimate for oxidized black liquor BPR is in Fig. 7. For solids contents below 50%, use the oil-free system data. Above 50% solids content, use the liquor oil system data.

Although the BPR estimate is thought adequate for evaporation equipment design, it is not sufficient for exact thermodynamic characterization. New data taken in a single well-controlled system over the entire solids range are needed. No existing procedure or equipment is available for these precise measurements. New developments in both are essential.

P_V ΔH_V, ΔH_D ESTIMATES FOR UNOXIDIZED BLACK LIQUOR

Despite the limitations discussed above in these and other data, it is meaningful to obtain an order of magnitude estimate for vapor pressure and heats of vaporization and dilution. The approach was outlined earlier in Eq. (9) and (10).

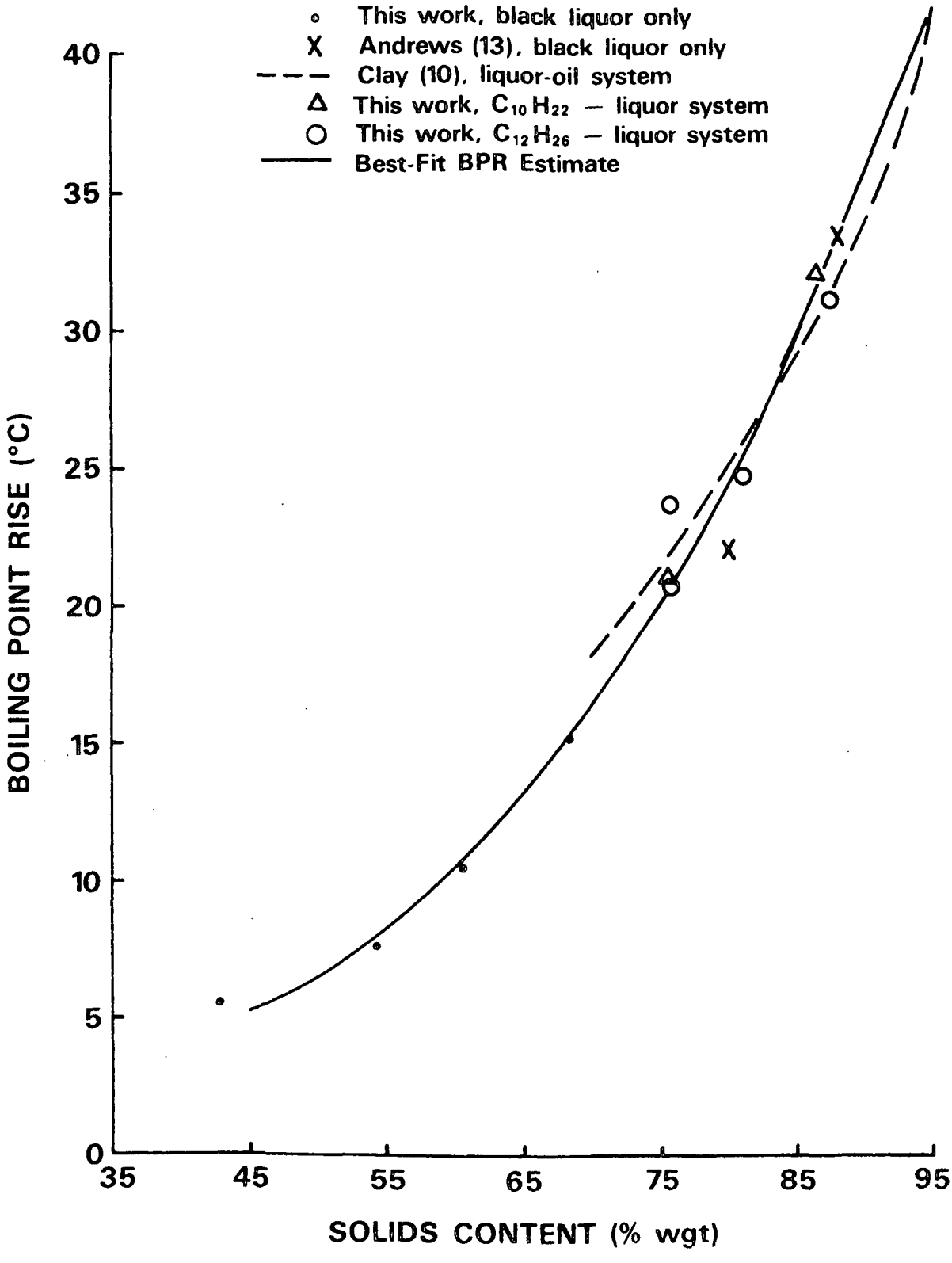


Figure 8. Best-fit estimate for black liquor BPR from combination of several data sources.

Table VII presents the estimates for three ranges of solids. The temperature data were adjusted via Fig. 8 to minimize inconsistencies.

The significant facts are that black liquor:

1. Heat of vaporization is greater than water
2. Heat of vaporization increases with solids content
3. Heat of dilution is negative, dilution is exothermic
4. Heat of dilution increases with solids content

Again, because of the multiple data sources, these are only trends. Numbers presented in Table VII are only estimates.

Two other sources (2,9) of vapor pressure data on black liquor can be used to obtain $\Delta\hat{H}_V$ and $\Delta\hat{H}_D$. They both show deviations increasing from water as solids increase. Kobe's (2) data are presented in Table VIII. One can draw the same conclusions as above from his work. Funk's (9) data show the reverse behavior, i.e., lower ΔH_V values and positive ΔH_D values. The apparent crystallization occurring in his work above 50% may have produced a different chemical system than under dynamic boiling conditions tested by Kobe (2) and this work. As mentioned above, more analytical testing is needed.

PROPOSED EXPERIMENTAL SYSTEM

The problems that have surfaced in this and other work suggest the following as system criteria.

1. Pure liquor-water system
2. Minimization of equilibration time, 2-3 hours maximum
3. Thin films or low inventory of liquor to minimize gradients

TABLE VII

ORDER OF MAGNITUDE ESTIMATION OF UNOXIDIZED BLACK LIQUOR VAPOR PRESSURE, HEAT OF VAPORIZATION AND HEAT OF DILUTION

Run No.	Oil Type	Solids, %	BPR_m,[a] °C	$\overline{BPR_m}$ / BPR_{bf}	T_{Bm}, °C	T_B^*,[b] °C	$\hat{P}_{BLm}$, mm Hg	$\Delta\hat{H}_{v,BL}$, kcal/ g mole H_2O	ΔC_p BPR, kcal/ g mole H_2O	$\Delta\hat{H}_{D,BL}$,[c] kcal/ g mole H_2O
6	C_{10}	75.5	21.0	+0.5	115.5	115.0	617.7			
5	C_{12}	75.7	20.7	0	118.7	118.7	704.5	10.6	0.1	-0.8
8	C_{12}	75.9	23.7	+3.0	121.7	118.7	703.2			
Ref. (13)	None	80	22.0	-2.3	154.0	156.3	2205			
								11.8	0.1	-2.0
5	C_{12}	81.4	24.7	-0.8	122.6	123.4	700.2			
6	C_{10}	86.1	32.0	+0.5	124.4	123.9	571.7			
5	C_{12}	87.4	31.2	-1.6	128.6	130.2	689.1	11.4	0.1	-1.6
Ref. (13)	None	88	33.3	0	165.3	165.3	2205			

[a] Subscript identification. m - measured, bf - best-fit from figure.
[b] $T_B^* = T_{Bm} - (BPR_m - BPR_{bf})$. Calculated best estimate of boiling temperature free of liquid-phase superheat.
[c] From equation (10) where $\Delta H_{v,W} = 9.94$ kcal/g mole H_2O.

4. Vapor recirculation to insure saturation
5. Measurement of both temperatures and pressures
6. Sealed system capable of pressure-vacuum operation
7. Temperature-controlled external environment to within ± 0.1°C
8. Ability to run isopiestic comparative checks with known salt solutions in the same chamber as the liquor
9. Continuous automatic recording equipment on all signals and holdup problems
10. Work carried out in as small a sample cell as possible to minimize leak potential
11. Pretreatment techniques to remove dissolved gases

TABLE VIII

BLACK LIQUOR P-T DATA AND IMPLIED HEAT OF VAPORIZATION AND HEAT OF DILUTION ESTIMATES FROM KOBE (2)

Solids, %	Temperature,[a] °C	Pressure, mm Hg	$\hat{\Delta H}_v$, kcal/g mole H_2O	ΔCp BPR, kcal/g mole H_2O	$\hat{\Delta H}_D$,[b] kcal/g mole H_2O
35	79.5	300	10.46	0.05	-0.57
	102.8	760			
63	87.6	300	10.55	0.02	-0.66
	111.8	760			

[a]These points taken from the best-fit line presented by Kobe on ln P vs. 1/T plot.
[b]From Eq. (10) where $\Delta H_{v,W}$ = 9.94 kcal/g mole H_2O.

One system that will meet these requirements is as follows. Liquor fills the voids of a fine mesh screen or some other equipment to extend its surface. Several of these aliquots are suspended in a cell where water vapor is recirculated via a pump/fan inside the cell. NaOH solution can be used to wet one screen for isopiestic tests. Several calibrated fine wire thermocouples are embedded in the screens for T_B measurement. The vapor temperature is measured at several points within the cell via fine wire thermocouples. A solid state pressure sensor is located within the cell. All inner cell connections to the outside environment are solid wires. The entire cell is immersed in the temperature-controlled bath. A cross check of data from this system with the oil dispersion data of this work will assure no spurious behavior such as found by Funk (9).

CONCLUSIONS

Development and evaluation of an oil dispersion technique for boiling point rise (BPR) measurements of unoxidized black liquor proved useful over the solids content range of 75 to 85%. Application on oxidized liquors is limited to 50-63%. Dispersion and superheat problems limit the applicable range of this method. A fairly extensive, but not exhaustive, literature search did not reveal any developed alternate technique applicable to a highly viscous and potentially precipitative aqueous solution analogous to black liquor.

A best-fit estimate of the BPR for unoxidized black liquor is presented over the range of 40 to 95% solids content. The best-fit estimate of BPR for partially oxidized liquor covers the range 43 to 63% solids content. These estimates are thought adequate enough for preliminary design of evaporation equipment operating within this range. The dependency determined shows an accelerated increase in unoxidized black liquor BPR at solids contents greater than 55%. The predicted BPR for solids contents of 70 and 85% are 16.5 and 30°C, respectively. Data from the oil dispersion technique, this work's oil-free liquor data, and other published sources were combined to yield this best-fit estimate. Liquor oxidation significantly increases the BPR. The predicted BPR for oxidized liquor at 50% and 60% solids content are 12°C and 20°C, respectively. This is approximately a 100% increase in comparable values for unoxidized liquors. The developed experimental techniques and analyses can now be applied for BPR estimates on specific liquors.

Order of magnitude estimates for unoxidized black liquor vapor pressure and heats of vaporization and dilution were made. These show significant deviations from pure water. Lower vapor pressures are obtained as solids contents increased. Higher heats of vaporization than that of water are predicted. These trends produce negative values for the heats of dilution. That is, the dilution process is

exothermic. The same trends were found with the published data of Kobe (2). Except for the vapor pressure behavior, these trends are the reverse of those found by Funk (9). Funk's data are suspect.

A study of these and other data suggested a number of criteria that an improved P-T measurement system for black liquor should meet. Extensive development of both equipment and procedure will be required.

RECOMMENDATIONS

1. Initiate work to develop a P-T measurement system for black liquor thermodynamic property characterization
2. Until reliable data are obtained from such an improved system, use the best-fit values from this work for ultra-high solids content liquor BPR estimates
3. Discontinue procedural development and data collection on the oil dispersion BPR technique
4. Investigate causes for the high BPR in oxidized liquors

ACKNOWLEDGMENTS

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NOMENCLATURE

BPR	Boiling point rise, °C. See Eq. (6) and (8)
C_1, C_2	Constants in T-P equation (7)
ΔCp	Specific heat difference between liquid and vapor, $\frac{\text{kcal}}{\text{g mole } H_2O}$
ΔH_D	Heat of dilution, $\frac{\text{kcal}}{\text{g mole } H_2O}$ · ^ above indicates estimate only.
ΔH_v	Heat of vaporization, $\frac{\text{kcal}}{\text{g mole } H_2O}$ · ^ above indicates estimate only.
$P_i(T_j)$	Vapor pressure of component i at temperature T_j, mm Hg · ^ above indicates estimate only.
P_T	Total system pressure, mm Hg
R	Gas constant
T_j	Temperature at condition j, °C
T_B^*	Calculated best estimate of boiling temperature free of liquid-phase superheat, °C
$T_C^*(P_w)$	Saturated water vapor temperature at water vapor pressure P_w. Determined from steam tables, °C
Components, i	
	W = water
	O = oil
	BL = black liquor
	SOLN = NaCl or NaOH solutions
Conditions, j	
	B = boiling
	C = condensing
	X = solids percent, %
Other Subscripts,	m measured
	bf best-fit from figure 6
	v vapor

THE INSTITUTE OF PAPER CHEMISTRY

David T. Clay
Research Associate
Recovery Group
Chemical Sciences Division

Thomas M. Grace
Group Leader, Recovery
Pulping Sciences
Chemical Sciences Division